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(54) DISPERSION LIQUID OF COPPER FINE-PARTICLE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a dispersion liquid of copper fine-particles having particle diameters of less than 200 nm.

SOLUTION: This dispersion liquid is obtained by suspending a copper compound having the particle diameter of less than 200 nm, in a polyol solvent, and subsequently reducing it at a lower temperature than 150°C and in an atmosphere of pressurized hydrogen.

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CLAIMS

[Claim(s)]
[Claim 1]Copper-particles dispersion liquid which make a polyol solvent come to contain copper particles which have the particle diameter below 200 nm.
[Claim 2]The copper-particles dispersion liquid according to claim 1, wherein this polyol solvent is a diethylene glycol.
[Claim 3]A manufacturing method of copper-particles dispersion liquid given in either of claim 1 or 2 obtaining by carrying out reduction processing of the copper compound which has the particle diameter below 200 nm under application-of-pressure hydrogen at temperature of less than 150 ** succeedingly after being suspended in a polyol solvent.
[Claim 4]A manufacturing method of the copper-particles dispersion liquid according to claim 3, wherein these copper compounds are copper I oxide and a cupric oxide.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to the copper-particles dispersion liquid used for the use of conductive paste, conductive ink, etc. in the mounting field of electronic equipment.
[0002]
[Description of the Prior Art]Conventionally, as for the copper-particles dispersion liquid used for the use of conductive paste, conductive ink, etc. in the mounting field of electronic equipment, reduction of filler size is needed in connection with the densification of wiring density in recent years. There are methods, such as a physical method and the chemical method, in the preparation method of copper particles. Although the manufacturing method of the copper particles which have the particle diameter of 100 nm or less with gas evaporation is publicly known in a physical method (JP,3-34211,A), in order to prevent the condensation between copper particles by this method, Copper particles need to be covered with alcohol and organic ester (all [alpha **TERUPINE], SHITORONE Norian, methyl oleate, and glyceride linolate) whose carbon numbers are five or more. Since they have long chain alkyl bulky in three dimensions or an annular skeleton, these covering organic matters have the insufficient contact between copper particles, when using this particle as a filler of copper-particles dispersion liquid, for example for this reason. Although it is also possible to heat and to remove a covering organic matter, there is a problem of needing about 400 ** or the elevated temperature beyond it in that case.
[0003]There is the method of on the other hand returning a copper compound with reducing agents, such as hydrazine, into a solution as a chemical preparation method. However, since cohesive force strong among the copper grain children who created works, this method cannot create the copper particles which have the particle diameter below 200 nm without addition of protective polymer etc. That is, conductivity is insufficient even if it can respond to the densification of wiring density. Although the method of obtaining copper particles by the method of carrying out heating reduction of the copper compound in a polyol solvent in the boiling point (it is 198 ** when ethylene glycol is used for polyol) of polyol is also publicly known (JP,4-24402,B), By this method, in order to use the dissolution-deposit reaction of the

copper compound under an elevated temperature, the particle diameter of the copper particles obtained becomes large, and cannot obtain the copper particles which have the particle diameter below 200 nm. That is, even if this method is enough as conductivity, by it, it cannot respond to the densification of wiring density.

[0004]Although the method of carrying out hydrogen reduction of the copper compound by ordinary pressure is also proposed (JP,64-47801,A), by this method, 150 ** or the high reaction temperature beyond it is usually needed. At the reaction in such elevated temperatures, since the copper particles to generate condense easily, the copper particles which have the particle diameter below 200 nm cannot be obtained.

[0005]

[Problem(s) to be Solved by the Invention]That is, an object of this invention is to provide the copper-particles dispersion liquid which have the particle diameter below 200 nm without spoiling the original conductivity of copper.

[0006]

[Means for Solving the Problem]In order that this invention person may solve an aforementioned problem, as a result of advancing examination wholeheartedly, an ultrafine particle of a copper compound which has the particle diameter below 200 nm, It was suspended in a polyol solvent, and found out that it could respond to densification of **** density, without a copper grain child's dispersion liquid produced by carrying out reduction processing using hydrogen under a specific temperature and a pressure spoiling the original conductivity of copper, and this invention was completed.

[0007]Namely, copper-particles dispersion liquid, wherein copper particles which have the particle diameter below 200 nm are distributing this invention to a polyol solvent, After being suspended in a polyol solvent, succeedingly a copper compound which is related with copper-particles dispersion liquid, wherein this especially polyol solvent is a diethylene glycol, and has the particle diameter below 200 nm at temperature of less than 150 **. It is related with a manufacturing method of copper-particles dispersion liquid obtaining by carrying out reduction processing under application-of-pressure hydrogen.

[0008]This invention is explained in detail below. It is characterized by a copper grain child with a particle diameter of less than 200 nm distributing copper-particles dispersion liquid of this invention to a polyol solvent. Copper particles of this invention have a globular form, a cubic shape, or the shape of a polyhedron form, and when it limits further, they have 1 nm or more less than 200 nm of 1-nm or more particle diameter below 100 nm. Content in the copper whole dispersion liquid of more than 0.01 mass % is [more than 0.01 mass % / less than 90 mass %] less than 85 mass % still more preferably.

[0009]Polyol which can be used for copper-particles dispersion liquid of this invention as a solvent has two or more hydroxyl groups in a molecule, is a compound which is a solution in a room temperature, and are a polyethylene glycol, a polypropylene glycol, alkylene glycol, glycerol, etc. Since this invention is a reaction using reducing power of hydrogen although it is known that itself has reduction nature and the reducing power changes greatly with differences in molecular structure when polyol is heated at an elevated temperature, there is no restriction

in reducing power of polyol.

[0010]Ethylene glycol with viscosity low in a room temperature, a diethylene glycol, A 1,2-propanediol, 1,3-propanediol, 1,2-butanediol, Although what has a small carbon number is preferred as for 1,3-butanediol, 1,4-butanediol, 2,3-butanediol, etc., it is usable also in what has big carbon numbers, such as pentanediol, hexandiol, octanediol, and a polyethylene glycol. One kind of these polyol solvents may be used as an independent solvent, and two or more polyol solvents may be mixed and it may use as a mixed solvent. The most desirable solvent in a polyol solvent is a diethylene glycol.

[0011]Next, a manufacturing method of copper-particles dispersion liquid of this invention is explained. Copper-particles dispersion liquid of this invention are suspended in a polyol solvent in a copper compound which has the particle diameter below 200 nm, carry out reduction processing using hydrogen under a specific temperature and a pressure, and are obtained.

[0012]Hereafter, it explains for details. As a copper compound which can be used for this invention, they are the first copper compound, for example, copper I oxide, a cuprous chloride, the first copper of bromination, a cuprous iodide, the first copper of sulfuric acid, the first copper of nitric acid, and the first copper of acetic acid. As the second copper compound, a cupric oxide, the second copper of hydroxylation, a cupric chloride, the second copper of bromination, the second copper of iodination, cupric sulfate, the second copper of nitric acid, cupric acetate, the second copper of azidation, etc. are illustrated, for example. As a more desirable thing, copper I oxide and a cupric oxide which do not contain halogen ion can be mentioned in these copper compounds.

[0013]In this invention, it is characterized by particle diameter of the above-mentioned copper compound being particle diameter below 200 nm. It is also possible for these to use a commercial item and to compound using a publicly known synthesizing method. for example, a way particle diameter heats and compounds an acetylacetonate copper complex at about 200 ** in a polyol solvent as a synthesizing method of copper I oxide which is less than 200 nm is publicly known (an ANGEBANTE Kem international edition -- two volumes No. 40) p. 359 or 2001. If particle diameter of a copper compound which is a raw material exceeds 200 nm, copper particles below 200 nm cannot be obtained by reduction processing.

[0014]In this invention, an ultrafine particle of the above-mentioned copper compound is first distributed in a polyol solvent. As a method of distributing a copper compound in a polyol solvent, a general method of distributing a copper compound granular material in a solution can be used. For example, an supersonic method, the mixer method, the 3 rolling method, the ball mill method, etc. can be mentioned. Especially desirable things are an supersonic method and the ball mill method especially. Usually, it distributes combining plurality of these dispersion means. These distributed processing may be performed at a room temperature, in order to lower viscosity of a solvent, may be heated and may be performed.

[0015]Although there is no restriction in particular in weight of a copper compound ultrafine particle distributed in a polyol solvent, since a granular material to mix is an ultrafine particle which has big surface area, it is the conditions exceeding 90wt% and it is impossible to create uniform dispersion liquid. It is also possible to omit distributed processing by compounding an

ultrafine particle of a copper compound which has the particle diameter below 200 nm in a polyol solvent.

[0016]A copper compound distributed in a polyol solvent by an above-mentioned method is contacted in hydrogen in a reaction vessel, by applying heat, carries out reduction processing of the copper compound, and compounds copper particles. Contact with hydrogen is performed by being filled up with hydrogen to a predetermined pressure, after inactive gas, such as nitrogen, fully replaces oxygen in a reaction vessel using a vacuum pump using a pressure-proof reaction vessel. Although a pressure of hydrogen and quantity of heat to apply change depending on particle diameter of a copper compound ultrafine particle which is a raw material, a pressure to apply needs to be larger than atmospheric pressure. Preferably, it is larger than atmospheric pressure, and it is a pressure of less than 10 MPa, is larger than atmospheric pressure still more preferably, and is a pressure of less than 8 MPa. Since particles will become is easy to be returned if particle diameter of a copper compound ultrafine particle which generally serves as a raw material becomes small, a reduction reaction progresses by a low-pressure hydrogen atmosphere. If application-of-pressure hydrogen is used, since generally applied quantity of heat can be made small, it is more desirable.

[0017]The range of less than 150 ** of reaction temperature is less than 120 ** still more preferably. If particle diameter of a copper compound ultrafine particle used as a raw material generally becomes small, there may be little quantity of heat to apply. If there is too much quantity of heat to apply, condensation will progress between copper particles to generate and particle diameter of copper particles which generate a copper compound which has the particle diameter below 200 nm even if also as a raw material will become larger than 200 nm. Even if reduction processing of this invention makes a reaction atmosphere a mixed atmosphere of inactive gas, such as nitrogen, argon, and helium, and hydrogen, it does not interfere. Since existence of oxygen promotes elution of a copper ion from a copper compound, it is not preferred.

[0018]

[Embodiment of the Invention]Next, although an example explains this invention still in detail, this invention should not be limited at all by these examples. Each particle diameter of the copper compound particles of a statement in the following examples and a comparative example and a copper grain child was measured with the Horiba laser dispersion type particle-size-distribution plan (LA-920). It checked that the ultrafine particle in the dispersion liquid obtained by hydrogen treatment was copper with the Rigaku International Corporation X-ray diffractometer (Rigaku-RINT 2500).

[0019]

[Example 1] 0.3 g of copper acetate (made by Wako Pure Chemical Industries, Ltd.) was suspended to 50 ml of diethylene glycols (made by Wako Pure Chemical Industries, Ltd.), 0.5 ml of water was added, the pyrogenetic reaction was carried out at 190 ** for 3 hours, and copper I oxide dispersion liquid with a mean particle diameter of 80 nm were obtained. After having put these dispersion liquid into the reactor made from stainless steel (autoclave), and putting in the MAGUNE tick stirring child for stirring and removing oxygen in a reactor using a

vacuum pump, it was filled up with hydrogen in the container so that it might become a pressure of 4.4MPa. Stirring an inside with a magnetic stirrer for 5 hours in the oil bath set as 70 **, the reactor was overheated and copper-particles dispersion liquid were obtained. The mean particle diameter of the obtained copper particles was 75 nm.

[0020]

[Example 2] 1 g of CuO nano particles (made by C.I. Kasei, Inc.) which have the mean particle diameter of 30 nm were added to 50 ml of diethylene glycols, and the ultrasonic dispersion machine and the ball mill dispersion machine performed distributed processing. After putting the obtained dispersion liquid into autoclave and removing oxygen in a reactor using a vacuum pump, it was filled up with hydrogen in the container so that it might become a pressure of 3.9MPa. Stirring an inside with a magnetic stirrer for 5 hours in the oil bath set as 70 **, the reactor was overheated and copper-particles dispersion liquid were obtained. The mean particle diameter of copper particles was 50 nm.

[0021]

[Example 3] Copper I oxide dispersion liquid with a mean particle diameter of 120 nm were obtained by stirring further copper I oxide dispersion liquid with a mean particle diameter of 80 nm obtained by the same operation as Example 1 for one week at a room temperature. After putting these dispersion liquid into autoclave and removing oxygen in a reactor using a vacuum pump, it was filled up with hydrogen in the container so that it might become a pressure of 1.2MPa. Stirring an inside with a magnetic stirrer for 2 hours in the oil bath set as 102 **, the reactor was overheated and copper-particles dispersion liquid were obtained. The mean particle diameter of the obtained copper particles was 94 nm.

[0022]

[Comparative example 1] Except that hydrogen pressure was atmospheric pressure, it reacted on the same conditions as Example 3, but copper I oxide particles were not returned and copper-particles dispersion liquid were not obtained.

[0023]

[Comparative example 2] Except that reaction temperature was 200 **, it reacted on the same conditions as Example 1. Although copper I oxide particles were returned, copper became floc with the size of an about 1-mm angle, and sedimented, and copper-particles dispersion liquid were not obtained.

[0024]

[Effect of the Invention]In the method by this invention, since the copper-particles dispersion liquid which have the particle diameter below 200 nm can be compounded without needing additives, such as a covering organic matter and protective polymer, the conductive paste for the wiring density in which the insulating material ingredient was reduced, and conductive ink can be provided.

[Translation done.]